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Assessing a solids-biased density-gradient functional for actinide metals

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Recent developments of new electron exchange and correlation functionals within density-functional theory include a solids-biased modification of the popular Perdew-Burke-Ernzerhof (PBE) GGA referred to as PBEsol. The latter is claimed to remove a bias toward free-atom energies and therefore better suited for equilibrium properties of densely-packed solids and surfaces. We show that PBEsol drastically worsens the equilibrium properties of the actinide metals compared to PBE and produce results closer to that of the von Barth-Hedin (BH) local density approximation. The PBEsol atomic volume of δ-Pu is 12% and 14% smaller than PBE and experimental values, respectively. Also iron is found to have the incorrect ground state phase assuming the PBEsol. These results show the difficulty in improving the GGA in a general fashion even when the application is restricted to solids. We comment on the possibility of producing a unique functional that is applicable to solids as well as to finite-sized systems such as atoms and molecules.

Efficient calculations of ground states for solids and molecules using density-functional theory (DFT) [1, 2] coupled with approximations of the electron exchange and correlation functionals (E_{xc}) have been very practical for several decades. Although the approach has some fundamental problems, which we discuss below, its successes when comparing to experimental data are too numerous to list. Generally it produces realistic lattice constants and binding energies for many elements, alloys, and compounds including transition metals [3].

It was early discovered that the more primitive form of approximation of the E_{xc}, that depends explicitly on the local electron density (local density approximation, LDA), has a tendency towards over binding. This deficiency is reflected in too small LDA atomic volumes for all transition metals [3] as well as the early actinides [4]. An advanced form of the E_{xc} includes gradient terms of the electron density as well. The first widely used general gradient approximation (GGA) to do this is due to Perdew and coworkers [5] which we will call PW91 hereafter. Ozolins and Körling [3] found PW91 to substantially improve on the LDA for equilibrium volumes and bulk moduli of non-magnetic transition metals. It was also discovered [6] that PW91 predicts the correct body-centered-cubic (bcc) ferromagnetic ground state of iron, something that the LDA fails to do. Both for α-cerium and the actinide metals [4, 7] PW91 was shown to be far superior to the LDA as well. PW91 was made simple in the so-called PBE [8] which retains the general features of the PW91 while having a less complex formulation at the cost of not fulfilling some non-essential exact conditions.

These GGAs certainly improve upon the LDA in many instances but over time it has become clear that they overcorrect the chronic LDA overbinding for some simple metals, ionic solids, and transition elements [9]. The overcorrection for the solids is attributed to an inherent bias toward the description of free-atom energies and the remedy is to eliminate this bias in a new functional PBEsol [9]. PBEsol is slightly tweaked to better correspond to the LDA in the sense that it restores the electron-density gradient expansion of the exchange energy [2] that is accurate for slowly varying densities. Consequently, the performance of PBEsol is closer to the LDA and thus producing better lattice constants for 18 solids [9].

The new PBEsol is a hopeful candidate for a more accurate E_{xc} and an aid for a better DFT description of solids in general. One worry, however, is that it might do worse in metals where PW91 strongly improve upon the LDA. The present paper explore this risk by focusing on the light actinide metals thorium through plutonium (atomic numbers 90 to 94) for which the PW91 indeed is a great upgrade over the LDA [4].

The early actinides are similar to the early d-transition metals in that valence electrons occupy chemically bonding band states that are contracting the lattice when proceeding through higher atomic numbers. For the actinides the major difference in terms of bonding is the much narrower $5f$ bands compared to the d bands of the transition metals. These narrow bands support distortions of the lattice giving rise to increasingly complex and deformed crystal structures traversing the series. The narrow bands also depart more strongly from the concept of slowly varying electron densities to which PBEsol is explicitly tuned.

In Fig. 1 we show calculations of the atomic volumes (V) for the elemental solids Th-Pu together with room temperature experimental data. The computations are for the correct crystal structures, non-magnetic, and include spin-orbit interaction. The technical details are similar to calculations for the actinides we have done in the past [10]. We have chosen the Janak *et al.* parameterization [11] of the von Barth and Hedin [12] E_{xc} to represent the LDA treatment (BH). All theoretical results have been modified due to thermal expansion. We have done this by using the experimental linear coefficient of thermal expansion, α, so that $V(T) = V(0)[1 + 3\alpha T]$ where T is the temperature chosen to be 300 K. Notice that the PBEsol results are relatively close to that of the BH but very far from the experimental data and on average 6.6% too small. PBE and PW91 are nearly identical and much closer to experiments. The PW91+OP treatment also includes orbital polarization (OP) that is an electron correlation similar to the spin-orbit interaction and a generalization of Hund's second rule of an atom. The OP is known to be important for plutonium [13] but has a small effect on Np and is negligible for uranium and the lighter actinides (not shown). The PW91 has an average error of about 1.6% which reduces to 1.2% when OP is accounted for.

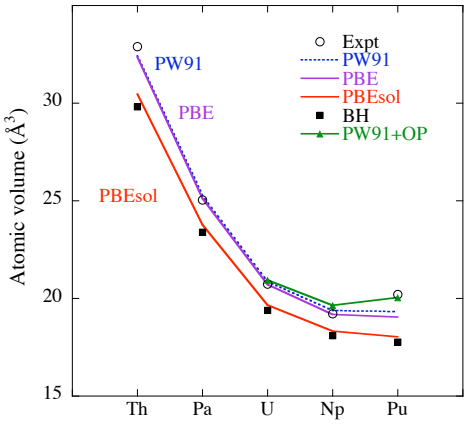

FIG. 1. Calculated atomic volumes, corrected for room temperature (see text) for the light actinides using various E_{xc} functionals. The calculations include spin-orbit coupling but no spin polarization. Orbital polarization (OP) is important for Pu and non-negligible for Np, but can be ignored for Th-U.

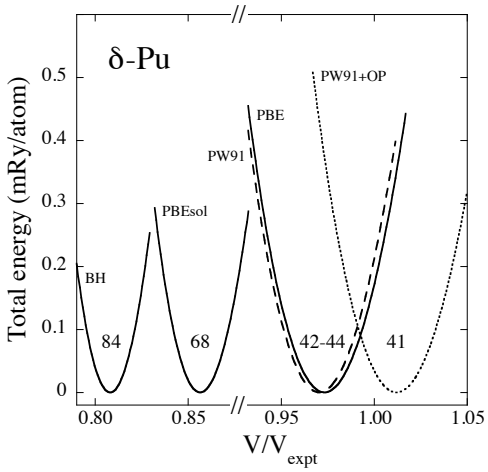

FIG. 2. Calculations similar to those in Fig. 1 but allowing spin polarization in a paramagnetic (disordered) phase (see text and Ref. [15]). The volumes (V) are scaled with the experimental (25 Å^3) volume. The bulk moduli for each treatment is shown in units of GPa. Notice that the x-axis has been contracted to better display the curves.

Although experimentally plutonium has not been proven to be a magnetic material [14], conventional DFT predicts formation of spin and orbital magnetic moments in Pu and the high-temperature δ phase in particular. We have argued recently that within DFT δ-Pu is best described as a paramagnet with disordered spin and anti-parallel orbital moments of similar magnitude [15]. In Fig. 2 we show calculations assuming the aforementioned DFT model with the same functionals as in Fig. 1. The experimental equilibrium volume (V_{expt}) for δ-Pu is 25 Å^3 and used to scale the x-axis in Fig. 2. Notice also that the x-axis is contracted to better fit all total-energy curves within one plot. As is the case for the light actinides, the new PBEsol dramatically worsens the agreement with experiment for δ-Pu, although it is better than the LDA. Nevertheless, the predicted PBEsol volume is almost 15% too small, while both PBE and PW91 are much closer to the measured volume. Very good agreement is obtained when also OP is included (PW91+OP). Perfect agreement is not expected because temperature effects are difficult to include and are ignored in these calculations. The PBEsol bulk modulus (68 GPa) is more than twice the experimental one ($\sim$ 30 GPa) while PBE and PW91 are both considerably closer ($\sim$ 40 GPa).

Clearly, the newly proposed PBEsol [9] is disappointing for the actinide metals. The very grave failure for the magnetic δ-Pu is particularly worrisome because one of the great successes of PW91 is the correct *magnetic* ground state of iron. We have therefore investigated also the magnetic bcc and non-magnetic hexagonal close-packed (hcp) phases of iron with these same functionals. In the upper panel of Fig. 3 we show the PBE total energy for the magnetic bcc (full line) and non-magnetic hcp (dotted) phases as a function of atomic volume. Clearly this functional correctly predicts the correct ground state of iron as is expected from previous reports for PW91 [6]. The equilibrium volume compares rather well with experimental data (vertical dashed line). The transition pressure obtained from the PBE total energies (common enthalpy) is about 14.4 GPa which is a little higher than that of a corresponding PW91 (11.9 GPa not shown) treatment. Unfortunately, in the middle panel, PBEsol shows the lowest total energy for the non-magnetic hcp phase even though the bcc ferromagnetic phase has only slightly higher total energy. The LDA (in the lower panel) also favors, more strongly than PBEsol, the non-magnetic phase, which is an established fail-

ure of the LDA [16].

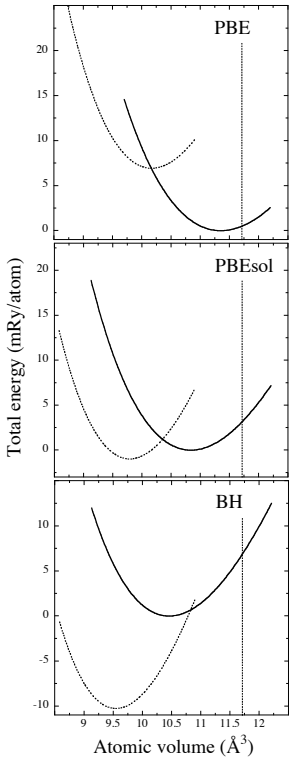

FIG. 3. PBE (upper panel), PBEsol (middle panel), and BH (lower panel) total energies for non-magnetic hcp (dashed) and magnetic bcc (full) iron as a function of atomic volume. Vertical dashed line represents the experimental atomic volume for iron. Only the PBE treatment (and PW91 not shown) predicts the correct ground state.

Nearly two decades have passed since the widely used and rather successful PW91 functional was presented. It improved the description of f-electron elements substantially and also predicted the correct ground state of the important metal iron. On these accounts and perhaps others the proposed PBEsol shows an unsatisfying performance. This revelation and the fact that any GGA formulation of the E_{xc} cannot satisfy, simultaneously, accurate atomic exchange energies and that of a slowly varying electron density [9, 17] leads us to believe that one must consider other avenues for DFT in the future.

One approach consists of the most recently proposed and hence most advanced functionals that tend to be of the hybrid type. Here one considers exchange terms determined by various procedures and includes each with weights deemed pertinent to particular applications. The exchange terms are needed in order to correct for the presence of self-interaction that is present in the Coulomb energy calculated in the form of the Hartree term. It appears, however, that this procedure often fails to lead to reliable results beyond those used to test it when deciding on the nature of the hybrid.

It is well known that self-interaction is exactly removed by one exchange term constructed from the orbitals calculated by the Kohn-Sham equations. As in the methodology of exact exchange and the so-called optimized effective potential (OEP) method[18] we suggest the inclusion of just this functional, but with one difference. The functional is to be treated together with the Hartree term allowing the calculation of the Coulomb energy in terms of the pair density. This produces a functional that is fully consistent with the nature of the Coulomb energy as an expectation value of the Coulomb operator with respect to the wave function (Slater determinant) determined by the Kohn-Sham equations.

We are currently investigating methodologies for obtaining the functional derivative of the pair density with respect to the density and expect to report on our efforts as results are obtained.

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